

# V.E.11 Molecular-Scale, Three-Dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions

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## Objectives

1. Demonstrate that non-platinum group metal catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes. (Year 1)
2. Incorporate catalysts into polymer binders of composite electrodes for the construction of membrane electrode assemblies (MEAs) to demonstrate that this is an effective matrix for testing of new catalysts. (Year 2)
3. Demonstrate that the three-dimensional structure of polymer-coated electrocatalyst layers can offset slower kinetics of the catalyst centers when compared with two-dimensional platinum or non-platinum catalysts. (Year 3)
4. Demonstrate that significant stability of the matrix is possible. (Year 3)
5. Demonstrate the design, synthesis and scale up of new catalysts capable of performance that is superior to platinum group metals. (Year 4)

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Performance
- (E) System Thermal and Water Management
- (B) Cost
- (A) Durability

## Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst – 300 A/cm<sup>3</sup>
- Cost <\$3/kW
- Durability >5,000 hours (>120°C)
- Electrochemical area loss <40%
- Electrochemical support loss <30 mV after 100 hrs @ 1.2 V

## Accomplishments

- Developed electrochemical screening methods for new catalysts using classical electrochemical methods.
- Developed synthetic methods to prepare new catalysts.
- Developed modeling procedures for prediction of catalyst activity on a molecular level.
- Modified polymer synthesis methods to provide attachment of catalysts to polymers.
- Undertaken preliminary study of polymer ink formulation for non-Nafion<sup>®</sup> binders for composite electrode fabrication for MEAs.



## Introduction.

Although proton exchange membrane (PEM) fuel cells are relatively efficient energy conversion devices

(~50%), there still remains considerable interest in improving the performance while reducing the cost. An area of study that can lead to greater efficiencies while reducing costs is that of the electrocatalysts and particularly the catalysts used for oxygen reduction where the sluggish kinetics leads to inefficient conversion of the energy to heat rather than electricity. The heat generation imposes extra costs due to system complexity to handle both heat and water management. The use of platinum and other platinum group metal catalysts adds further expense. There therefore is considerable interest in developing alternative catalysts that are less expensive and also more efficient. Gasteiger and co-workers [1] have provided a very thorough review of the benchmark activities required for Pt, Pt-alloy and non-Pt catalysts for oxygen reduction and describes in detail different approaches to catalysis of this important reaction.

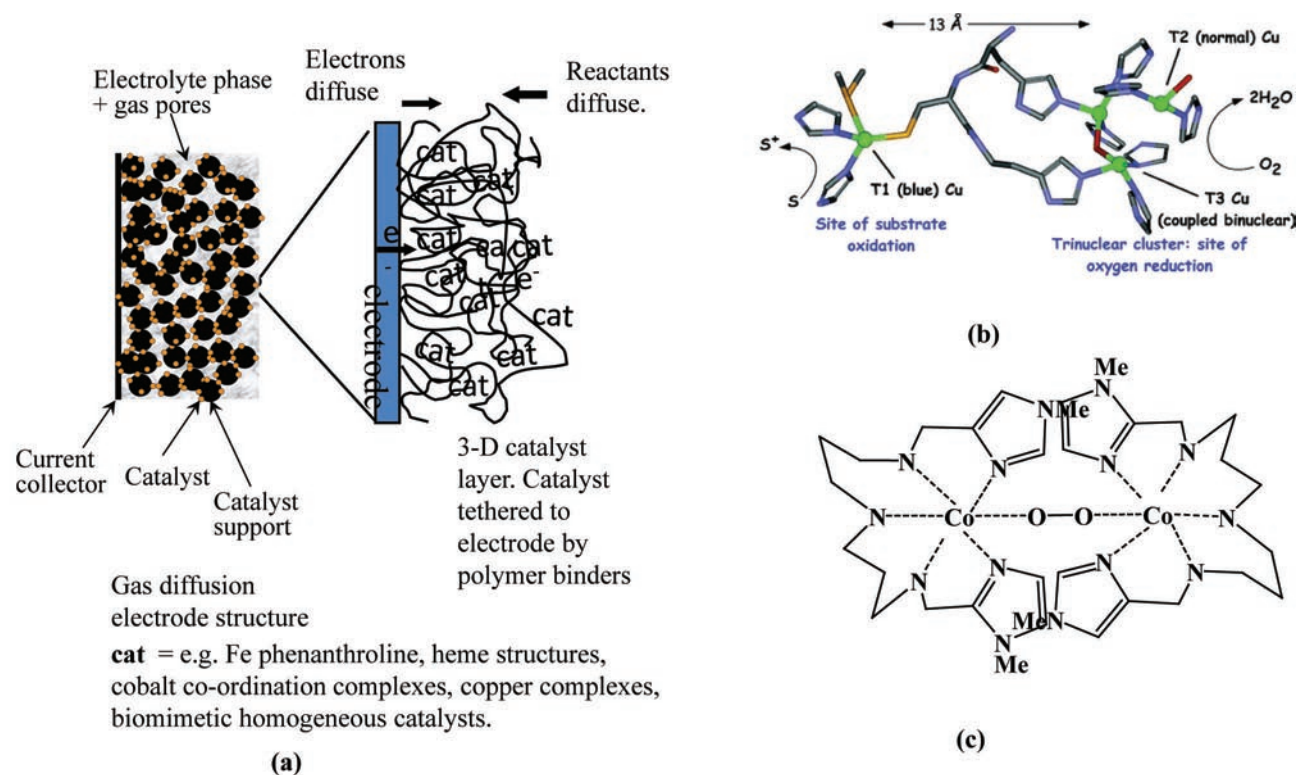
Methods have been reported to prepare non-precious metal catalysts that involve a curious procedure whereby a rather complicated molecule such as a metal porphyrin or a complex such as iron phenanthroline is adsorbed on carbon and then heated to over 800°C to form the catalyst [2-5]. In some cases the carbon support is treated with nitrogenous compounds at high temperature followed by addition of metal ions such as Fe or Co. Although the resulting electrodes are often highly porous with very high surface areas the resulting catalyst layers on the electrode surface are two-dimensional in nature. With these non-platinum catalyst structures the kinetics of oxygen reduction are much less rapid than commercially available platinum on carbon electrode. It is thought that the density of the non-platinum catalytic sites is insufficient to sustain the desired reaction. With the porphyrin catalysts, for example, their poor solubility results in strong adsorption on to the carbon support and insufficient loading of catalyst as well as possible deactivation of the metal center. Since it has been shown by Heller [6], for example, that the copper laccase enzyme obtained from biological sources is capable of supporting current densities for oxygen reduction of 0.5 mA/cm<sup>2</sup> at a planar carbon electrode with a polarization of only 70 mV, it appears that nature has evolved a catalyst that can outperform platinum. Electrode structures are desired which can allow incorporation of such catalytic species into MEAs, which increase in the surface concentration of the electrocatalysts and which allow the activity of the catalyst to be retained while it is incorporated into the PEM fuel cell engineering platform.

## Approach

Homogeneous redox catalysis has been the center of considerable academic attention for several decades now. A recent review by Saveant [7] provides an extensive overview of the topic and includes methods

of tethering catalysts close to the electrode surface. These methods suggest ways to incorporate into fuel cell MEAs electrocatalysts that mimic the enzyme catalyst centers and may lead to better performance at reduced cost. Figure 1(a) shows a schematic of a gas diffusion electrode structure typically used in a PEM fuel cell. The electrode usually consists of catalyst nanoparticles (e.g. Pt) dispersed on carbon support particles bound together by a polymeric ionomer material (e.g. Nafion<sup>®</sup>) on a current collector such as a gas diffusion layer (GDL) which is electronically conductive. The polymer therefore acts as a binder to hold the electrode together and as an electrolyte to transport hydrogen ions to and from the electrode surface. This structure has been designed to optimize the transport of electrons, hydrogen ions, substrate and product to and from the catalyst surface and generally the overall thickness of the electrode layer is about 10 μm. A thicker electrode introduces mass transport limitations that degrade performance. The right hand side of Figure 1(a) shows a schematic blow up of the surface of the electrode where the polymer binder layer is used to bind homogeneous catalysts close to but not right on the surface. This structure allows the use of a variety of catalysts some of which are listed in Figure 1(a) and could be used to tether even an enzyme catalyst such as the copper laccase structure shown in Figure 1(b) or an oxygen binding catalyst such that shown in Figure 1(c). It has been shown (see reference [7] and references therein) that the optimum thickness of the polymer layer can be up to 500 nm thick which would be equivalent to about 100 monolayers of the catalyst on the electrode surface. This thickness of the polymer layer on the electrode particle surface represents little if any increase of the overall thickness of the gas diffusion electrode and hence it is possible to greatly increase the areal density of catalysts on the electrode without increasing the electrode thickness, a concern that was well described by Gasteiger et al. [1].

The operation of the polymer-tethered catalyst layer can appear puzzling to some and the reader is referred to reference [7] for further details. Suffice to say here is that the electrons are transferred from the surface of the current collector by means of an electron hopping mechanism between redox centers as well as by movement of the polymer tethered catalyst back and forth towards the electrode. Therefore the polymer in addition to binding the catalyst must also provide the means to transport protons and ions which can neutralize the charging of the polymer layer. This charging process may indeed be a rate determining step but so also may be the rate of diffusion of the oxygen into the layer or the actual rate of reaction of the catalyst with the substrate and the subsequent dissociation rate of the catalyst and product. In this the catalyst is no different from a metal surface catalyst. What is very different about this approach is that the catalyst center



**FIGURE 1.** Molecular Catalyst Incorporation in Gas Diffusion Electrodes (a) Schematic of a gas diffusion electrode showing molecular catalysts tethered to the polymer binder layer used to hold the electrode together; (b) Structure of the catalytic center of copper laccase; (c) Structure of an oxygen-binding cobalt complex.

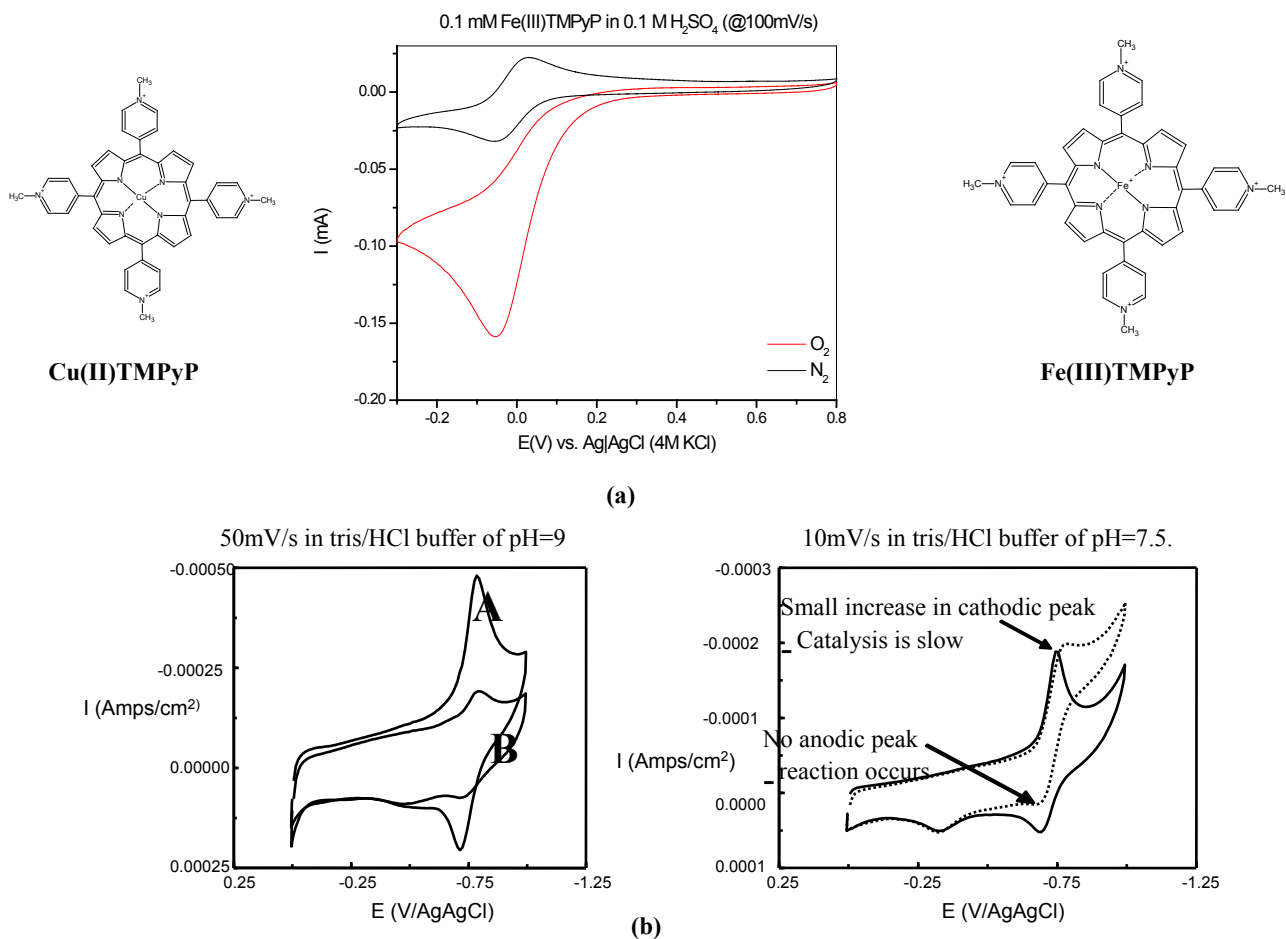
is effectively a homogeneous catalyst and it may be approached from all directions by the substrate. This provides a geometric advantage for the catalyst center over a surface bound center and can provide an increase in catalytic activity of an order of magnitude or more. This effect combined with the multilayer effect can provide up to three orders of magnitude increase purely due to geometric effects on a molecular scale that hold the potential to make up for the large catalyst area and potentially slower intrinsic kinetics.

The third and most important advantage of the approach is that the catalyst functions essentially as a homogeneous catalyst that can be thoroughly characterized in solution. This makes design and synthesis of the catalysts much more straightforward since they can be studied without resort to surface analysis techniques and to the invocation of surface effects that are poorly understood. Thus, catalysts can be designed from first-principles based on well-known chemistry and physics. The structures of the catalytic centers are understood since the catalysts are synthesized and characterized by classical electrochemical methods in solution thereby avoiding some of the difficulties that have arisen from surface bound catalysts. The catalysts are then incorporated into polymers for coating on electrode surfaces and

again the behavior can be characterized by simple electrochemical methods prior to incorporating the polymer-bound catalysts into composite electrodes for MEAs. This last step is critical for the project and represents the Go/No-Go decision point that allows the flow of more efficient catalysts into the PEM fuel cell platform for practical use.

## Results

Figure 2 illustrates the process of catalyst screening and incorporation into polymers using classical cyclic voltammetry techniques. Figure 2(a) shows the voltammetric response of a representative iron porphyrin complex (Fe(III)TMPyP) which is soluble in aqueous perchloric acid solution due to the quaternized pyridinium groups. The Fe(III)/Fe(II) redox couple is shown to be a chemically and electrochemically reversible couple under nitrogen (blue line) indicating fast electron transfer between the carbon electrode and the iron complex. Upon saturation of the solution with oxygen the red curve is observed which shows the increase of reduction current due to reaction of the Fe(II) complex with oxygen. The extent of the increase in current is dependent upon the relative concentration of catalyst and substrate and the sweep rate used to perform



**FIGURE 2.** Screening of ORR Catalysts by Cyclic Voltammetry (a) Voltammogram of Fe(III)TMPyP under nitrogen and in the presence of oxygen at carbon; (b) Voltammograms of Cp\*Rhodium catalyst bound to a polymer layer deposited on carbon under nitrogen and in the presence of substrate.

the experiment. From measurements such as these it is possible to actually determine the rate constants of the catalytic reactions [7]. The corresponding copper complex was also active for catalysis of the oxygen reduction reaction (ORR). A point to note here is that these complexes show some stability in acid at least kinetically. Many complexes are immediately decomposed by acid and these results show that the instability can be mitigated. Whether this will be long enough to be useful in a fuel cell remains to be seen.

Figure 2(b) shows the voltammetry of a catalyst which has been attached to a polymer and the polymer layer coated on a carbon electrode. In this case the catalyst is a rhodium Cp\* organometallic complex which has carbon-metal bonds that are not susceptible to acid cleavage. The left hand voltammograms show the response of the catalyst in two cases. One is with a thin layer of polymer (B) and the other is with a thick layer (A). Integration of the current peaks gives the charge due to the catalyst and hence one can calculate the density of catalyst sites on the electrode. The peak shapes are symmetrical and characteristic of a thin layer

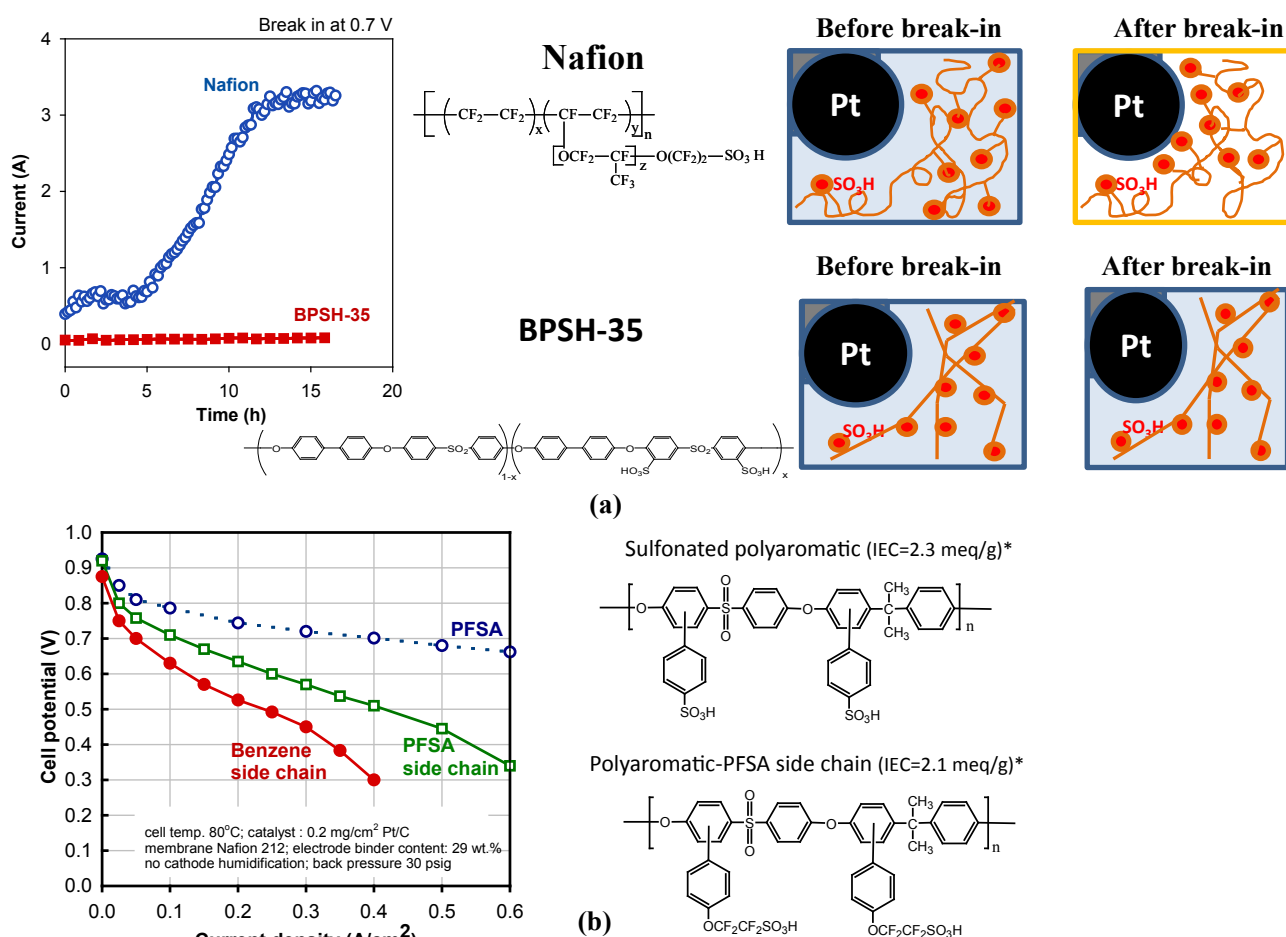
of reactant on the electrode surface. These shapes vary with the sweep rate and from such experiments it is possible to estimate the rate of polymer charging [8] as well as diffusion rates through the polymer layer. The voltammogram on the right hand side of Figure 2(b) shows the effect of the addition of a substrate molecule which is reduced by the catalyst. One can see in this case a small increase in the reduction current and a reduction in the height of the oxidation current peak which indicates a reaction occurs between catalyst and substrate but the small increase in reduction current indicates a slow reaction. In this case comparison with the behavior of the catalyst in solution shows that the activity of the catalyst is reduced and this was attributed to low availability of hydrogen ions for the reaction in the polymer matrix that was used. This illustrates the importance of the polymer properties in providing for transport of protons to the site of the reaction. The polymer used in this case was not a polyelectrolyte with no ion transport functionalities. For future work in this project it will be important to choose polymer matrices with this capability and for this use will be made of

polymers from the high temperature membrane project funded by the Department of Energy [9].

These initial results from simple electrochemical experiments demonstrate the importance of the polymer structure that is used to tether the catalysts to the electrode. Preparation of Pt-catalyst MEA electrodes with polymers other than Nafion® is shown in Figure 3 to illustrate this point. The break-in current of a Nafion® electrode is compared with that of an electrode prepared with a polyether polysulfone binder electrolyte. The cartoons on the right hand side of Figure 3(a) represent what is thought to be happening. During break-in the Nafion® polymer is mobile enough to move close to the surface and provide adequate contact. The polyether polysulfone is a stiff polymer and is unable to move close to the electrode surface and hence the break-in is very poor. Figure 3(b) shows polarization curves for three different polymer binders. Once again there is a distinct correlation between the flexibility of the polymer backbone or side chain and the performance in an MEA. These results emphasize the importance of

polymer structure on the ability to fabricate a workable MEA electrode and hence attention to polymer structure and properties is critical to the success of this project. In order to demonstrate the feasibility of MEA fabrication readily available catalysts will be selected for incorporation into the polymers. The presence of the catalysts will alter the properties of the polymers and hence considerable experimentation will be required to determine the best formulations and fabrication procedures. This is best done with easily obtainable catalytic centers.

Figure 4 illustrates some syntheses of copper complexes which will be examined for catalytic activity using the classical electrochemical procedures. These are related to complexes already described by Gewirth et al. [10]. In addition to synthesis and characterization experimentally these complexes will also be modeled by molecular calculation to compare theory and experiment. Validation of the modeling procedure by such experiments will allow new catalysts to be



**FIGURE 3.** Effect of Polymer Structure on MEA Performance (a) Comparison of break-in of MEA electrodes prepared with Nafion® and polyether polysulfone; (b) Comparison of polarization curves of MEAs prepared with different polymer binders in the gas diffusion electrode.

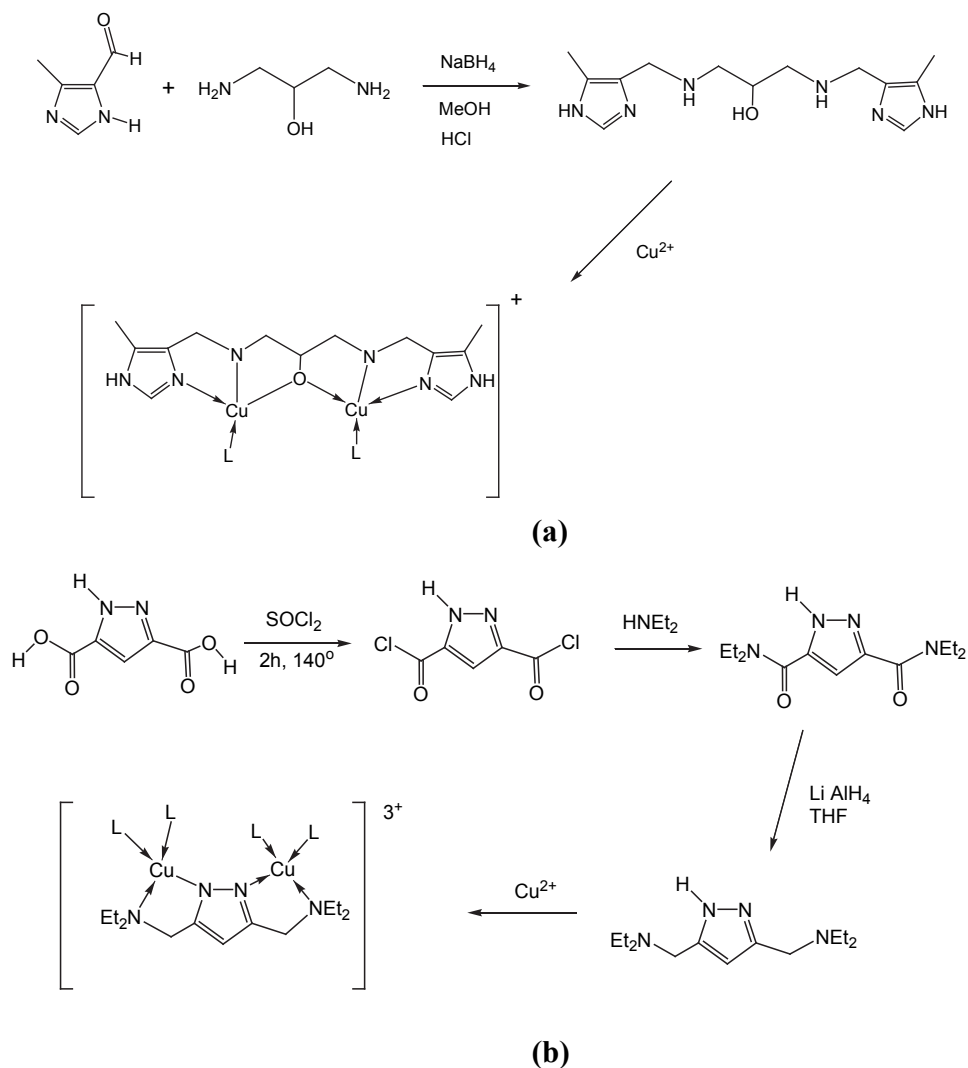


FIGURE 4. Synthetic Routes under Development to Two Types of Copper Catalysts

designed, synthesized and characterized to improve the efficiency of the ORR reaction.

## Conclusions and Future Directions

### Conclusions

- Classical electrochemical methods can be used to characterize the catalytic activity of homogeneous ORR catalysts.
- The structure of the polymer matrix must be designed to provide adequate charge and mass transport to the catalyst centers.
- The polymer binder properties are critical for MEA fabrication.

### Future Directions

- Increase screening rates of available catalysts to select promising candidates that are stable to acid.
- Develop quantitative measurements of catalytic activity in solution and in polymer-solvent mixtures that are representative of an MEA electrode environment.
- Develop synthetic procedures for attachment of catalysts to polymer binders.
- Continue to explore the properties required of polymer binders to facilitate fabrication of MEAs and study how the presence of catalytic centers changes these properties.
- Design and prepare new catalysts.
- Develop and validate molecular modeling techniques

## FY 2010 Publications/Presentations

1. “Molecular-scale, Three-dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions”, John Kerr, DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, June 08, 2010, Washington, D.C., presentation FC11.

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